

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|   |           |  |
|---|-----------|--|
| <b>(51) International Patent Classification<sup>6</sup> :</b><br><b>C08L 33/02, 67/02</b>   | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 96/00751</b><br><b>(43) International Publication Date:</b> 11 January 1996 (11.01.96)   |
| <b>(21) International Application Number:</b> PCT/US95/08062<br><b>(22) International Filing Date:</b> 27 June 1995 (27.06.95)<br><br><b>(30) Priority Data:</b><br>08/268,215 29 June 1994 (29.06.94) US<br><br><b>(71) Applicant:</b> S. C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403-5011 (US).<br><b>(72) Inventors:</b> CALHOUN, Glenn, C.; 3533 Ascot Drive, Racine, WI 53406 (US). OBUCHOWSKI, David, B.; 710 South Street, Racine, WI 53402 (US). POPLI, Rakesh, K.; 4902 Singing Trees Drive, Racine, WI 53406 (US).<br><b>(74) Agents:</b> RAKOCZY, Richard, E. et al.; Patent Section, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403-5011 (US). |           | <b>(81) Designated States:</b> CA, FI, MX, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> POWDER COATING COMPOSITIONS  |           |  |
| <b>(57) Abstract</b><br><br>Thermosetting powder coating compositions comprising blends of acid functional-group containing acrylic polymers and acid functional-group containing polyesters that are compatible or partially compatible and possess superior weatherability characteristics, excellent mechanical properties, and long-term storage stability.   |           |  |

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |                                       |    |                          |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AT | Austria                  | GB | United Kingdom                        | MR | Mauritania               |
| AU | Australia                | GE | Georgia                               | MW | Malawi                   |
| BB | Barbados                 | GN | Guinea                                | NE | Niger                    |
| BE | Belgium                  | GR | Greece                                | NL | Netherlands              |
| BF | Burkina Faso             | HU | Hungary                               | NO | Norway                   |
| BG | Bulgaria                 | IE | Ireland                               | NZ | New Zealand              |
| BJ | Benin                    | IT | Italy                                 | PL | Poland                   |
| BR | Brazil                   | JP | Japan                                 | PT | Portugal                 |
| BY | Belarus                  | KE | Kenya                                 | RO | Romania                  |
| CA | Canada                   | KG | Kyrgyzstan                            | RU | Russian Federation       |
| CF | Central African Republic | KP | Democratic People's Republic of Korea | SD | Sudan                    |
| CG | Congo                    | KR | Republic of Korea                     | SE | Sweden                   |
| CH | Switzerland              | KZ | Kazakhstan                            | SI | Slovenia                 |
| CI | Côte d'Ivoire            | LI | Liechtenstein                         | SK | Slovakia                 |
| CM | Cameroon                 | LK | Sri Lanka                             | SN | Senegal                  |
| CN | China                    | LU | Luxembourg                            | TD | Chad                     |
| CS | Czechoslovakia           | LV | Latvia                                | TG | Togo                     |
| CZ | Czech Republic           | MC | Monaco                                | TJ | Tajikistan               |
| DE | Germany                  | MD | Republic of Moldova                   | TT | Trinidad and Tobago      |
| DK | Denmark                  | MG | Madagascar                            | UA | Ukraine                  |
| ES | Spain                    | ML | Mali                                  | US | United States of America |
| FI | Finland                  | MN | Mongolia                              | UZ | Uzbekistan               |
| FR | France                   |    |                                       | VN | Viet Nam                 |
| GA | Gabon                    |    |                                       |    |                          |

WO 96/00751

PCT/US95/08062

- 1 -

TITLE

POWDER COATING COMPOSITIONS

5 BACKGROUND OF THE INVENTION

Powder coating compositions are widely used in a variety of industrial applications. For example, they have been used as paints or coatings for automobile surfaces, electrical appliances, and building materials. In most of these applications, it is highly desirable to have powder coating compositions that have a proper balance of weatherability characteristics, mechanical properties, and storage stability. Powder coating compositions which have the desired balance of properties can withstand harsh environmental conditions, possess high impact resistance and great flexibility, and exhibit long-term storage stability.

20 Powder coating compositions based on acrylic polymers have superior weatherability characteristics relative to compositions based on polyesters. However, polyester coating compositions have improved mechanical properties over acrylic coating compositions. Prior attempts to provide powder coating compositions containing blends of acrylic polymers and polyesters have resulted in compositions having a good balance of

WO 96/00751

PCT/US95/08062

- 2 -

weatherability and mechanical properties, but poor in storage stability.

- The present inventors have discovered thermosetting powder coating compositions comprising blends of acrylic polymers and polyesters that are compatible or partially compatible and possess superior weatherability characteristics, excellent mechanical properties, and long-term storage stability.
- Therefore, the thermosetting powder coating compositions of this invention are uniquely effective as paints or coatings in a wide variety of industrial applications.

SUMMARY OF THE INVENTION

A first embodiment of the present invention provides a thermosetting powder coating composition comprising:

- (A) 5 to 95 percent by weight of an acid functional-group containing acrylic polymer having a number average molecular weight of 500 to 10,000 and a glass transition temperature ( $T_g$ ) of 30 to 100°C.;
- (B) 95 to 5 percent by weight of at least one amorphous acid functional-group containing polyester that is compatible or partially compatible with said acrylic polymer, wherein said polyester has a number average molecular weight of 2,000 to 10,000, a glass transition temperature of 0 to 75 °C. and is polymerized from compounds consisting essentially of acid functional-group containing compounds and hydroxyl functional-group containing compounds or derivatives thereof, wherein at least 80 mole percent of said acid functional-group containing compounds is cyclohexanedicarboxylic acid; and

WO 96/00751

PCT/US95/08062

- 3 -

(C) an effective amount of a cross-linking agent;

wherein said percent by weight is based on the total weight of said acrylic polymer and said polyester.

5

A second embodiment of the present invention provides a thermosetting powder coating composition comprising:

(A) 70 to 95 percent by weight of an acid functional-  
10 group containing acrylic polymer having a number average molecular weight of 500 to 10,000 and a glass transition temperature ( $T_g$ ) of 30 to 100°C.;

(B) 5 to 30 percent by weight of at least one semi-  
15 crystalline acid functional-group containing polyester that is compatible or partially compatible with said acrylic polymer, wherein said polyester has a number average molecular weight of 2,000 to 10,000, a melting temperature ( $T_m$ ) of greater than 25°C. and is  
20 polymerized from at least 90 mole percent of aliphatic compounds based on the total number of moles of compounds in the polyester; and

(C) an effective amount of a cross-linking agent;  
25

wherein said percent by weight is based on the total weight of said acrylic polymer and said polyester.

#### BRIEF DESCRIPTION OF THE DRAWING

30

Fig. 1 is a plot of QUV weathering data of powder coating compositions according to the present invention and a conventional acrylic polymer coating composition.

WO 96/00751

PCT/US95/08062

- 4 -

5                    DETAILED DESCRIPTION OF THE INVENTION

The acid functional-group containing polyester according to the present invention has a number average molecular weight of 2,000 to 10,000. The molecular weight is determined by gel permeation chromatography (GPC) using polystyrene standards. When the number average molecular weight is smaller than 2,000, the storage stability of the blend of the acrylic polymer and the polyester becomes poor. Storage stability is a very important characteristic for powder coating compositions. When the storage stability is poor, the polymer blend, when stored for an extended period of time, agglomerates into chunks and clumps that are difficult to break into fine powder by simple shaking or low shear. When the number average molecular weight is greater than 10,000, the polymer blend flow is poor, resulting in films that are not smooth.

In the first embodiment of the present invention, the thermosetting powder coating composition comprises 95 to 5 percent by weight, preferably 30 to 10 percent by weight, based on the total weight of the polyester and the acrylic polymer of at least one acid functional-group containing polyester and 5 to 95 percent by weight, preferably 70 to 90 percent by weight, of an acid functional-group containing acrylic polymer. The acid functional-group containing polyester is amorphous and is polymerized from acid functional-group containing compounds and hydroxyl functional-group containing compounds or derivatives thereof, wherein at least 80 mole percent of the acid functional-group containing compounds is cyclohexanedicarboxylic acid. Preferably, the acid functional-group containing compounds and the hydroxyl functional-group containing compounds are di- or tri- functional compounds. When the acid functional-group containing compounds are less

SUBSTITUTE SHEET (RULE 26)

WO 96/00751

PCT/US95/08062

- 5 -

than 80 mole percent cyclohexanedicarboxylic acid, the resultant polyester may either have a low  $T_g$  or become incompatible with the acrylic polymer. Preferably, the acid functional-group containing compounds in the polyester are 100 percent cyclohexanedicarboxylic acid, such as 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, and 1,2-cyclohexanedicarboxylic acid, or its anhydride.

10 The polymerization may be conducted by condensing the acid functional-group containing compounds with the hydroxyl functional-group containing compounds. Examples of the hydroxyl functional-group containing compounds include polyols such as ethylene glycol, 15 propylene glycol, butylene glycol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane, cyclohexanedimethanol, and bisphenol A, with cyclohexanedimethanol being the preferred polyol. Examples of acid functional-group containing compounds 20 other than cyclohexanedicarboxylic acid include aliphatic and/or aromatic polycarboxylic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, succinic acid, undecanedioic acid, terephthalic acid, isophthalic acid, trimellitic acid, 25 and phthalic acid, and anhydrides thereof. Preferably, the other acid functional monomers are selected from aliphatic dicarboxylic acids with 6 to 12 carbon atoms.

The amorphous acid functional-containing polyester has 30 an acid number of about 10 to 55. The amorphous acid functional-containing polyester has a glass transition temperature of 0 to 75 °C. The  $T_g$  of the polymer may be measured by differential scanning calorimetry (DSC) at a heating rate of 20°C. per minute with  $T_g$  taken at the 35 middle point of the inflection curve.

SUBSTITUTE SHEET (RULE 26)

WO 96/00751

PCT/US95/08062

- 6 -

In accordance with the second embodiment of the present invention, the powder coating composition comprises 5 to 30 percent by weight, preferably 10 to 20 percent by weight, based on the total weight of the polyester and the acrylic polymer of at least one semi-crystalline acid functional-group containing polyester and 70 to 95 percent by weight, preferably 80 to 90 percent by weight, of an acid functional-group containing acrylic polymer. When the powder coating composition comprises more than 30 percent by weight of the semi-crystalline polyester, the hardness of the resultant coating decreases. The crystallinity of the polyester contributes to the storage stability of the coating composition. The semi-crystalline acid functional-group containing polyester has an acid number of about 10 to 55. The semi-crystalline acid functional-group containing polyester has a melting point of at least 25°C, preferably between 50 to 100°C. When the melting point is below 25°C., the storage stability of the blend of the acrylic polymer and the polyester deteriorates. The melting point may be measured by differential scanning calorimetry. The semi-crystalline acid functional group-containing polyester usually has a low  $T_g$ , i.e., lower than 0 °C.

The semi-crystalline acid functional-group containing polyester is polymerized from at least 90 mole percent of aliphatic compounds based on the total number of moles of compounds in the polyester. Preferably, the polyester is polymerized from 100 percent aliphatic compounds. When the polyester is polymerized from less than 90 mole percent of aliphatic compounds, the compatibility of the polyester and the acrylic polymer is reduced. The polymerization may be conducted by condensing polycarboxylic acids with polyols. Suitable aliphatic polycarboxylic acids include adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic



WO 96/00751

PCT/US95/08062

- 7 -

5 acid, succinic acid, and undecanedioic acid.

Preferably, the aliphatic polycarboxylic acids are dicarboxylic acids with 6 to 12 carbon atoms. Suitable aliphatic polyols include ethylene glycol, propylene glycol, butylene glycol, 1,6-hexanediol, 1,4-

10 cyclohexanedimethanol, neopentyl glycol, diethylene glycol, and trimethylolpropane. Preferably, the aliphatic polyols are diols with 3 to 8 carbon atoms. Examples of other non-aliphatic polycarboxylic acids include trimellitic acid and phthalic acid, and  
15 anhydrides thereof, as well as isophthalic acid and terephthalic acid. Examples of other non-aliphatic polyols are bisphenol A derivatives, such as bisphenol A diacetate or adducts of bisphenol A and ethylene oxide, propylene oxide or combinations of such oxides.

20

The acid functional-group containing acrylic polymer in both embodiments according to the present invention has a number average molecular weight of 500 to 10,000 and a glass transition temperature of 30° to 100°C. The  
25 acrylic polymer is amorphous. The acid functional-group containing acrylic polymer has an acid number of about 40 to 240.

The acid functional-group containing acrylic polymer  
30 may be polymerized from acrylic acid and/or methacrylic acid ester monomers and ethylenically unsaturated acid functional-group containing monomers. Other ethylenically unsaturated copolymerizable monomers may also be added. Preferably, the acid functional-group  
35 containing acrylic polymer comprises 20 to 95 percent by weight of at least one acrylic or methacrylic acid ester monomers having from 1 to 20 carbon atoms, 5 to 30 percent by weight of at least one ethylenically unsaturated acid functional-group containing monomer,  
40 and 0 to 60 percent by weight of at least one other

WO 96/00751

PCT/US95/08062

- 8 -

5 ethylenically unsaturated copolymerizable monomer,  
based on the total weight of the monomers.

Examples of acrylic acid ester monomers include methyl  
acrylate, ethyl acrylate, n-propyl acrylate, isopropyl  
10 acrylate, n-butyl acrylate, and n-decyl acrylate.

Examples of methacrylic acid ester monomers include  
methyl methacrylate, ethyl methacrylate, n-propyl  
methacrylate, n-butyl methacrylate, isopropyl  
methacrylate, isobutyl methacrylate, n-amyl  
15 methacrylate, n-hexyl methacrylate, isoamyl  
methacrylate, allyl methacrylate, sec-butyl  
methacrylate, tert-butyl methacrylate, 2-ethylbutyl  
methacrylate, cinnamyl methacrylate, crotyl  
methacrylate, cyclohexyl methacrylate, cyclopentyl  
20 methacrylate, methallyl methacrylate, n-octyl  
methacrylate, 2-ethylhexyl methacrylate, 2-phenylethyl  
methacrylate, and phenyl methacrylate.

Examples of ethylenically unsaturated acid functional-  
25 group containing monomers include acrylic acid,  
methacrylic acid, crotonic acid, itaconic acid, fumaric  
acid, maleic acid, citraconic acid, and monoalkyl  
esters of unsaturated dicarboxylic acids. The  
preferred ethylenically unsaturated acid functional-  
30 group containing monomers are acrylic acid and  
methacrylic acid.

Examples of other ethylenically unsaturated  
copolymerizable monomers include vinyl aromatic  
35 monomers, such as styrene, alkyl-substituted styrenes,  
and chloro-substituted styrenes; nitriles, such as  
acrylonitrile; vinyl and vinylidene halides, such as  
vinyl chloride and vinylidene fluoride; and vinyl  
esters, such as vinyl acetate.

WO 96/00751

PCT/US95/08062

- 9 -

The acrylic polymer according to the present invention may be made by conventional free radical initiated polymerization. Suitable free radical initiators that may be employed include benzoyl peroxide, tert-butyl hydroperoxide, ditert-butyl peroxide, azobis(2-methylpropionitrile). Other well-known techniques such as emulsion polymerization, suspension polymerization, and bulk polymerization may also be used to make the acrylic polymer according to the present invention.

10

The thermosetting powder coating compositions according to the present invention contains an effective amount of a cross-linking agent. Preferably, the stoichiometric ratio is 0.7 to 1.5 moles of the reactive groups on the cross-linking agent relative to 1 mole of the acid functional groups in the polyester and the acrylic polymer. Most preferably, the stoichiometric ratio is 0.9 to 1.1 moles of the cross-linking reactive groups relative to one mole of the acid functional groups of the two polymers. Suitable cross-linking agents include low molecular weight aromatic or aliphatic epoxies, triglycidyl isocyanurate, activated hydroxyl containing compounds such as beta-hydroxyalkylamide and tris(2-hydroxyalkyl)isocyanurate, and amine-urea-formaldehyde and melamine-formaldehyde type resins.

25

The powder coating compositions according to the present invention may optionally contain additives that are typically incorporated into thermosetting powder coating compositions. These additives include pigments, dyes, anti-popping agents, flow control agents, powder flow additives, degassing agents, and light stabilizers. Particularly recommended are degassing agents which allow volatiles to escape from the film during baking and flow control agents which

30

35

WO 96/00751

PCT/US95/08062

- 10 -

prevent cratering of the finish. Benzoin is a highly preferred degassing agent.

#### INDUSTRIAL APPLICABILITY

5 The thermosetting powder coating compositions according to the present invention are prepared by melt blending the ingredients of the coating compositions. This can be accomplished by first blending in a high-intensity  
10 mixer, for example, a Welex mixer and then melt blending in a two-roll mill or a twin-screw extruder at a temperature of about 80°C. to 130°C. The milled samples or the extrudate are then cooled and ground into powder. The powder coating composition can then  
15 be deposited directly onto a variety of substrates, including metal such as steel or aluminum, glass, plastic, or fiber-reinforced plastic substrates. The deposition can be conducted by known techniques in the art such as electrostatically spraying or fluidized bed  
20 sintering. After the powder coating has been deposited on a substrate, the coated substrate is heated sufficiently to melt the coating and long enough to cure the coating. For example, a metal substrate could be heated at from 150°C. to 200°C. for about 10 to 30  
25 minutes to effect curing of the powder coating composition.

The following examples illustrate the preparation of various acid functional-group containing polyesters  
30 according to the present invention.

#### EXAMPLE A

An acid functional-group containing polyester was  
35 prepared by charging 1715.5 grams of 1,4-cyclohexane-dicarboxylic acid and 1284.5 grams of 1,4-cyclohexane-dimethanol as monomers to a 5 liter flask equipped with

WO 96/00751

PCT/US95/08062

- 11 -

stirring means, a thermometer, a nitrogen inlet and outlet, and a water removal apparatus. The water removal apparatus has a steam jacketed distillation column packed with glass beads, a Dean-Stark trap, and  
5 a condenser. Dibutyl tin oxide as a catalyst was then added to the flask at 0.1 weight percent of the total weight of the monomers. Triphenyl phosphite as a color stabilizer was added at 0.05 weight percent of the total weight of the monomers. A 0.2 L/minute flow of  
10 dry nitrogen was passed over the system to maintain an inert atmosphere and to assist the removal of water. The contents of the flask were heated to 155°C. and maintained at that temperature for twenty minutes. The temperature was then raised 10°C. to 165°C. and held  
15 there for another twenty minutes. This step-increase in temperature procedure was repeated until a temperature of 215°C. was reached. During this procedure, water was continuously removed. The contents of the flask were then held at 215°C. for nine  
20 hours before the resultant polyester was removed from the flask and cooled to room temperature. The polyester obtained had an acid number of 45 (in mg KOH/g polymer),  $T_g$  of 45°C., a number average molecular weight of 3,300 and a weight average molecular weight  
25 of 7,000.

## EXAMPLE B

An acid functional-group containing polyester was  
30 prepared in the same manner as in Example A, except that the monomers charged were 1607.8 grams of adipic acid, 1321.7 grams of 1,4-cyclohexanedimethanol, and 71.2 grams trimethylolpropane. The resultant polyester had an acid number of 44,  $T_m$  of 73°C., a number average  
35 molecular weight of 4,000, and a weight average molecular weight of 16,000.

WO 96/00751

PCT/US95/08062

- 12 -

5

## EXAMPLE C

An acid functional-group containing polyester was prepared in the same manner as in Example A, except that the monomers charged were 1986.1 grams of sebacic acid, 951.3 grams 1,6-hexanediol, and 62.6 grams trimethylolpropane. The resultant polyester had an acid number of 43,  $T_m$  of 60°C., a number average molecular weight of 4,000, and a weight average molecular weight of 16,000.

15

## EXAMPLE D

An acid functional-group containing polyester was prepared in the same manner as in Example A, except that the monomers charged were 1723.8 grams adipic acid, 1174.1 grams 1,6-hexanediol, and 77.3 grams trimethylolpropane. The resultant polyester had an acid number of 48,  $T_m$  of 47°C., a number average molecular weight of 5,000, and a weight average molecular weight of 20,000.

25

## EXAMPLE E

An acid functional-group containing polyester was prepared in the same manner as in Example A, except that the monomers charged were 288.6 grams adipic acid and 211.9 grams 1,4-cyclohexanedimethanol. The resultant polymer had an acid number of 29, a peak melting temperature  $T_m$  of 100°C, a number average molecular weight of 4,600, and a weight average molecular weight of 12,000.

35

WO 96/00751

PCT/US95/08062

- 13 -

# COMPARATIVE EXAMPLE A

An acid functional-group containing polyester was prepared in the same manner as in Example A, except that the monomers charged were 258.8 grams adipic acid and 241.3 grams 1,4-cyclohexanedimethanol. The resultant polyester has an acid number of 123,  $T_m$  of 90°C, a number average molecular weight of 1,700, and a weight average molecular weight of 3,000.

10

The following examples illustrate the preparation of the thermosetting powder coating compositions according to the present invention. In all of the following examples, the acid functional-group containing acrylic polymer is a copolymer of styrene/methyl methacrylate/butyl acrylate/acrylic acid in a weight ratio of 20/58/15/7 having a number average molecular weight of 5,800, a weight average molecular weight of 16,000,  $T_g$  of 68°C, and an acid number of 55.

20

## EXAMPLE 1

A powder coating composition was prepared from the following ingredients:

25

| Weight   | Ingredients                                      |
|----------|--|
| 108.00 g | Acid functional-group containing acrylic polymer |
| 27.00 g  | Polyester of Example A                           |
| 11.00 g  | Primid® XL-552 Crosslinker <sup>1</sup>          |
| 2.00 g   | Modaflow® III <sup>2</sup>                       |
| 1.00 g   | Benzoin  |

30

<sup>1</sup>Beta-hydroxyalkylamide manufactured by Rohm & Haas.

35

<sup>2</sup>Modaflow® III is an acrylate copolymer flow control agent manufactured by Monsanto.

WO 96/00751

PCT/US95/08062

- 14 -

The above ingredients were pre-mixed by visually checking for a powdery texture, i.e., the absence of any large chunks or clumps. A 2-Roll Mill was set at 130°C. and allowed to warm up for approximately 1 to 2  
5 hours. The pre-mixed sample was then introduced to the mill quickly, and allowed to melt before starting the timer. Thereafter, the sample was taken off every minute, folded, twisted, and passed between rollers. This was repeated five times. The milled sample was  
10 then ground and sieved through a 140 mesh screen. Due to the heat generated during grinding, it may be necessary to cool the sample during grinding. This will depend on the size of the sample and the grinding equipment used. The finely-divided, powder coating  
15 composition obtained was then electrostatically sprayed on a polished cold rolled steel BONDERITE® 1000 panel from Parker Chemical Company and baked for 25 minutes at 190°C. The properties of the resultant coating are reported in Table 1 below.

20

## EXAMPLE 2

A powder coating composition was prepared from the following ingredients:

25

| Weight     | Ingredients                                      |
|------------|--|
| 114.80 g   | Acid functional-group containing acrylic polymer |
| 13.50 g    | Polyester of Example B                           |
| 6.80 g     | Polyester of Example C                           |
| 30 11.80 g | Primid® XL-552 Crosslinker                       |
| 2.00 g     | Modaflow® III                                    |
| 1.50 g     | Benzoin  |

The powder coating composition was prepared in the same  
35 manner as Example 1, except that after grinding and sieving, the sample was placed in the freezer at a



WO 96/00751

PCT/US95/08062

- 15 -

temperature of between 0°C. to -10°C. for a minimum of two hours to develop crystallinity in the polyester component. The properties of the resultant coating are reported in Table 1 below.

5

## EXAMPLE 3

A powder coating composition was prepared from the following ingredients:

10

| Weight   | Ingredients                                      |
|----------|--|
| 114.80 g | Acid functional-group containing acrylic polymer |
| 6.80 g   | Polyester of Example C                           |
| 13.50 g  | Polyester of Example D                           |
| 11.78 g  | Primid® XL-552 Crosslinker                       |
| 2.00 g   | Modaflow® III                                    |
| 1.50 g   | Benzoin  |

15

The powder coating composition was prepared in the same manner as in Example 2. The properties of the resultant coating are reported in Table 1 below.

20

## EXAMPLE 4

A powder coating composition was prepared from the following ingredients:

25

| Weight   | Ingredients                                      |
|----------|--|
| 111.77 g | Acid functional-group containing acrylic polymer |
| 27.94 g  | Polyester of Example E                           |
| 15.78 g  | Primid® XL-552 Crosslinker                       |
| 2.27 g   | Modaflow® III                                    |
| 1.00 g   | Benzoin  |

30

35

WO 96/00751

PCT/US95/08062

- 16 -

The powder coating composition was prepared in the same manner as in Example 1. The properties of the resultant coating are reported in Table 1 below.

5 COMPARATIVE EXAMPLE 1

A powder coating composition was prepared from the following ingredients:

| 10       | <table><tr><th>Weight</th><th>Ingredients</th></tr><tr><td>134.80 g</td><td>Acid functional-group<br/>containing acrylic polymer</td></tr><tr><td>12.17 g</td><td>Primid® XL-552 Crosslinker</td></tr><tr><td>2.02 g</td><td>Modaflow® III</td></tr><tr><td>1.47 g</td><td>Benzoin</td></tr></table> | Weight | Ingredients | 134.80 g | Acid functional-group<br>containing acrylic polymer | 12.17 g | Primid® XL-552 Crosslinker | 2.02 g | Modaflow® III | 1.47 g | Benzoin |
|----------|--|--------|-------------|----------|---|---------|----------------------------|--------|---------------|--------|---------|
| Weight   | Ingredients  |        |             |          |   |         |                            |        |               |        |         |
| 134.80 g | Acid functional-group<br>containing acrylic polymer  |        |             |          |   |         |                            |        |               |        |         |
| 12.17 g  | Primid® XL-552 Crosslinker   |        |             |          |   |         |                            |        |               |        |         |
| 2.02 g   | Modaflow® III  |        |             |          |   |         |                            |        |               |        |         |
| 1.47 g   | Benzoin  |        |             |          |   |         |                            |        |               |        |         |

15 The powder coating composition was prepared in the same manner as in Example 1. The properties of the resultant are reported in Table 1 below.

20 COMPARATIVE EXAMPLE 2

A powder coating composition was prepared from the following ingredients:

| 25       | <table><tr><th>Weight</th><th>Ingredients</th></tr><tr><td>111.77 g</td><td>Acid functional-group<br/>containing acrylic polymer</td></tr><tr><td>27.94 g</td><td>Polyester of Comparative<br/>Example A</td></tr><tr><td>11.44 g</td><td>Primid® XL-552 Crosslinker</td></tr><tr><td>2.27 g</td><td>Modaflow® III</td></tr><tr><td>1.00 g</td><td>Benzoin</td></tr></table> | Weight | Ingredients | 111.77 g | Acid functional-group<br>containing acrylic polymer | 27.94 g | Polyester of Comparative<br>Example A | 11.44 g | Primid® XL-552 Crosslinker | 2.27 g | Modaflow® III | 1.00 g | Benzoin |
|----------|--|--------|-------------|----------|---|---------|---------------------------------------|---------|----------------------------|--------|---------------|--------|---------|
| Weight   | Ingredients  |        |             |          |   |         |                                       |         |                            |        |               |        |         |
| 111.77 g | Acid functional-group<br>containing acrylic polymer  |        |             |          |   |         |                                       |         |                            |        |               |        |         |
| 27.94 g  | Polyester of Comparative<br>Example A  |        |             |          |   |         |                                       |         |                            |        |               |        |         |
| 11.44 g  | Primid® XL-552 Crosslinker   |        |             |          |   |         |                                       |         |                            |        |               |        |         |
| 2.27 g   | Modaflow® III  |        |             |          |   |         |                                       |         |                            |        |               |        |         |
| 1.00 g   | Benzoin  |        |             |          |   |         |                                       |         |                            |        |               |        |         |

30 The powder coating composition was prepared in the same manner as in Example 1. The properties of the resultant coating are reported in Table 1 below.

WO 96/00751

PCT/US95/08062

- 17 -

TABLE 1

|                                   | Example 1 | Example 2 | Example 3 | Example 4 | Comparative Example 1 | Comparative Example 2 |
|-----------------------------------|-----------|-----------|-----------|-----------|-----------------------|-----------------------|
| Gloss (20/60) <sup>1/</sup>       | 63/93     | 61/87     | 60/87     | 63/88     | 60/90                 | 76/97                 |
| Impact Resistance: <sup>2/</sup>  |           |           |           |           |                       |                       |
| Direct (in.-lbs.)                 | 60        | 100       | 140       | 160       | 30                    | 160                   |
| Reverse (in.-lbs.)                | 20        | 20        | 60        | 140       | 10                    | 120                   |
| Mandrel Flexibility <sup>3/</sup> | Pass      | Pass      | Pass      | Pass      | Fail                  | Pass                  |
| Storage Stability <sup>4/</sup>   | 9         | 5         | 5         | 5         | 9                     | 1                     |
| Pencil Hardness <sup>5/</sup>     | HB        | HB        | HB        | HB        | H                     | HB                    |
| MEK Rubs <sup>6/</sup>            | 50        | 75        | 75        | 50        | >100                  | 100                   |
| Flow & Levelling <sup>7/</sup>    | 3         | 6         | 6         | 5         | 3                     | 8                     |
| Adhesion <sup>8/</sup>            | 5B        | 5B        | 5B        | 5B        | 4B                    | 5B                    |

SUBSTITUTE SHEET (RULE 26)

WO 96/00751

PCT/US95/08062

- 17/1 -

- 1/ Gloss was measured as reflectance (% reflected) from a surface using a glossometer set up for measurements at 20° and 60° angles.
- 2/ Impact resistance was measured with a du Pont Impact tester (1 in. diameter; 1 lb. mass). The coated panels were subjected to increasing amounts of impact until the coating cracked or delamination occurred. The panel was impacted on the coating side, i.e., direct impact, and on the side of the panel opposite the coating, i.e., reverse impact. The results are reported in inch-pounds and the film thickness is between 1.8 to 2.5 mils.
- 3/ Mandrel flexibility was determined by bending the coated panels on a conical mandrel. The breaking and delamination of the coated film from the panel are then determined by visual inspection. Delamination of the coatings from the panel is a failure.
- 4/ Storage stability was determined by placing a sample of the powder composition in a bottle and stored at 40°C for 7 days. Storage stability rating of 1 to 10 (10 being the best) was given to indicate the size of agglomerates and how easily agglomerates could be broken into fine powder by simple shaking or under a low shear.
- 5/ Pencil hardness was determined by taking pencil leads of increasing hardness and attempting to etch a scribe mark in the coating. The softest pencil which will etch the coating was reported as the pencil hardness of the film.
- 6/ MEK Rubs is a measure of the degree of cure and the chemical resistance of the coating to a solvent. This was determined by rubbing a cloth soaked in MEK (methyl ethyl ketone) under a 1 lb. weight on the coated panel. The rubs represent the number of strokes on the panel when the coating first started to be affected by the solvent.
- 7/ Flow and levelling was determined by visual inspection on a scale of 1 to 10.
- 8/ Adhesion was measured in accordance with the crosshatched adhesion test of ASTM D-3359-83.

SUBSTITUTE SHEET (RULE 26)

BEST AVAILABLE COPY

WO 96/00751

PCT/US95/08062

- 18 -

5 Each of the coated panels in Examples 1 to 3 and  
Comparative Example 1 were also subjected to the QUV  
Weathering Test by exposing the coated panels to  
alternating cycles of U.V. light and condensing  
humidity in a Q-U-V-Accelerated Weathering Tester  
10 manufactured by the Q-Panel Co. The U.V. light is  
generated with a UVB313 lamp (320-280 nanometers). The  
temperature of the condensing humidity cycle is 50°C.  
The gloss at 20° was measured as a function of QUV  
exposure time. The results are illustrated in Fig. 1.

15 While the present invention has been described with  
respect to what is presently considered to be the  
preferred embodiments, it is to be understood that the  
invention is not limited to the disclosed embodiments.  
20 The present invention is intended to cover various  
modifications and equivalent formulations included  
within the spirit and scope of the appended claims.

WO 96/00751

PCT/US95/08062

- 19 -

WHAT IS CLAIMED IS:

1. A thermosetting powder coating composition comprising:

(A) 5 to 95 percent by weight of an acid functional-group containing acrylic polymer having a number average molecular weight of 500 to 10,000 and a glass transition temperature ( $T_g$ ) of 30 to 100° C.;

(B) 95 to 5 percent by weight of at least one amorphous acid functional-group containing polyester that is compatible or partially compatible with said acrylic polymer, wherein said polyester has a number average molecular weight of 2,000 to 10,000, a glass transition temperature of 0 to 75°C. and is polymerized from compounds consisting essentially of acid functional-group containing compounds and hydroxyl functional-group containing compounds or derivatives thereof, wherein at least 80 mole percent of said acid functional-group containing compounds is cyclohexanedicarboxylic acid; and

(C) an effective amount of a cross-linking agent; wherein said percent by weight is based on the total weight of said acrylic polymer and said polyester.

2. A thermosetting powder coating composition according to Claim 1, wherein said acid functional-group containing compounds are 100 percent cyclohexanedicarboxylic acid or its anhydride.

3. A thermosetting powder coating composition according to Claim 1, wherein said polyester has an acid number of about 10 to 55.

4. A thermosetting powder coating composition according to Claim 1, comprising 70 to 90 percent by weight of said acid functional-group containing acrylic

WO 96/00751

PCT/US95/08062

- 20 -

polymer and 30 to 10 percent by weight of said acid functional-group containing polyester.

5. A thermosetting powder coating composition according to Claim 1, wherein said acid functional-group containing compounds and hydroxyl functional-group containing compounds are di- or tri-functional compounds.

6. A thermosetting powder coating composition according to Claim 1, wherein the stoichiometric mole ratio of the reactive groups on said cross-linking agent relative to the acid functional-groups on said acrylic polymer and said polyester is 0.7 to 1.5:1.

7. A thermosetting powder coating composition according to Claim 6, wherein said stoichiometric mole ratio is 0.9 to 1.1:1.

8. A thermosetting powder coating composition according to Claim 1, wherein said hydroxyl functional-group containing compounds are cyclohexanedimethanol.

9. A thermosetting powder coating composition comprising:

(A) 70 to 95 percent by weight of an acid functional-group containing acrylic polymer having a number average molecular weight of 500 to 10,000 and a glass transition temperature ( $T_g$ ) of 30 to 100° C.;

(B) 30 to 5 percent by weight of at least one semi-crystalline acid functional-group containing polyester that is compatible or partially compatible with said acrylic polymer, wherein said polyester has a number average molecular weight of 2,000 to 10,000, a melting temperature ( $T_m$ ) of greater than 25°C. and is polymerized from at least 90 mole percent of aliphatic

WO 96/00751

PCT/US95/08062

- 21 -

compounds based on the total number of moles of the compounds in the polyester; and

(C) an effective amount of a cross-linking agent;

wherein said percent by weight is based on the total weight of said acrylic polymer and said polyester.

10. A thermosetting powder coating composition according to Claim 9, wherein said semi-crystalline polyester is polymerized from 100 percent aliphatic compounds.

11. A thermosetting powder coating composition according to Claim 9, wherein said semi-crystalline polyester has a melting temperature of between 50 to 100°C.

12. A thermosetting powder coating composition according to Claim 9, wherein said polyester has an acid number of about 10 to 55.

13. A thermosetting powder coating composition according to Claim 9, comprising 80 to 90 percent by weight of said acid functional-group containing acrylic polymer and 20 to 10 percent by weight of said acid functional-group containing polyester.

14. A thermosetting powder coating composition according to Claim 10, wherein said polyester is polymerized by condensing aliphatic polycarboxylic acids with aliphatic polyols.

15. A thermosetting powder coating composition according to Claim 14, wherein said polycarboxylic acids are selected from dicarboxylic acids with 6 to 12 carbon atoms.



WO 96/00751

PCT/US95/08062

- 22 -

16. A thermosetting powder coating composition according to Claim 14, wherein said polyols are selected from diols with 3 to 8 carbon atoms.

17. A thermosetting powder coating composition according to Claim 9, wherein the stoichiometric mole ratio of the reactive groups on said cross-linking agent relative to the acid functional-groups on said acrylic polymer and said polyester is 0.7 to 1.5:1.

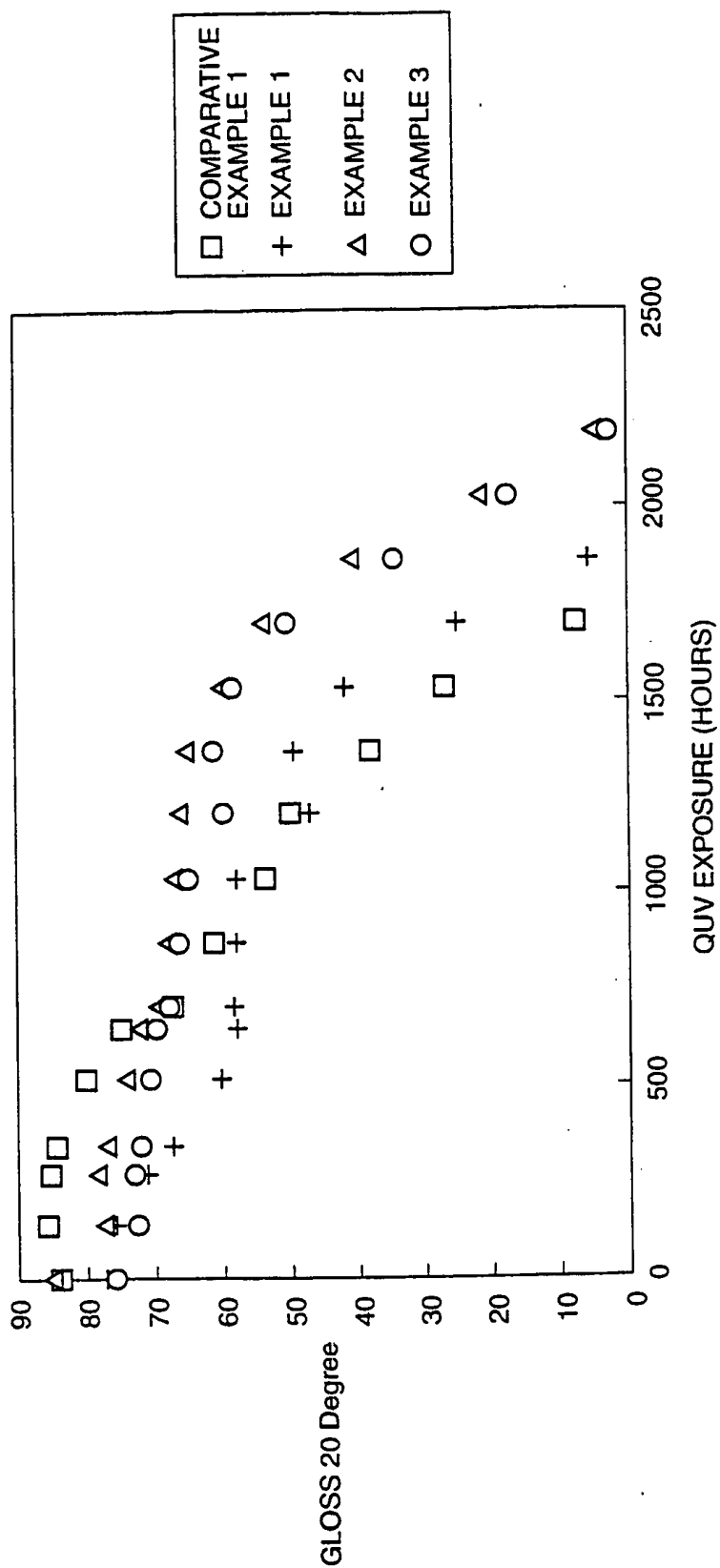
18. A thermosetting powder coating composition according to Claim 17, wherein said stoichiometric mole ratio is 0.9 to 1.1:1.

WO 96/00751

PCT/US95/08062

1 / 1

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/08062

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08L 33/02, 67/02

US CL : 525/176

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/176, 445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X         | US, A, 4,937,288, (PETTIT) 26 June 1990, see entire document.                      | 1-18                  |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

|   |     |  |
|---|-----|--|
| * Special categories of cited documents:  | * T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
| * A document defining the general state of the art which is not considered to be of particular relevance  | * X | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone   |
| * E earlier document published on or after the international filing date  | * Y | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| * L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | * & | document member of the same patent family  |
| * O document referring to an oral disclosure, use, exhibition or other means  |     |  |
| * P document published prior to the international filing date but later than the priority date claimed  |     |  |

Date of the actual completion of the international search

02 AUGUST 1995

Date of mailing of the international search report

12 OCT 1995

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PATRICIA SHORT

Telephone No. (703) 308-2351